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For

USE OF OXYHYDROXIDE COMPOUNDS FOR REDUCING
CARBON MONOXIDE IN THE MAINSTREAM SMOKE OF A CIGARETTE

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**Use of Oxyhydroxide Compounds for Reducing
Carbon Monoxide in the Mainstream Smoke of a Cigarette**

FIELD OF INVENTION

[001] The invention relates generally to methods for reducing the amount of carbon monoxide in the mainstream smoke of a cigarette during smoking. More specifically, the invention relates to cut filler compositions, cigarettes, methods for making cigarettes and methods for smoking cigarettes that involve the use of oxyhydroxide compounds, which decompose during smoking to produce one or more products capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide.

BACKGROUND

[002] Various methods for reducing the amount of carbon monoxide in the mainstream smoke of a cigarette during smoking have been proposed. For example, British Patent No. 863,287 describes methods for treating tobacco prior to the manufacture of tobacco articles, such that incomplete combustion products are removed or modified during smoking of the tobacco article. In addition, cigarettes comprising absorbents, generally in a filter tip, have been suggested for physically absorbing some of the carbon monoxide. Cigarette filters and filtering materials are described, for example, in U.S. Reissue Patent No. RE 31,700; U.S. Patent No. 4,193,412; British Patent No. 973,854; British Patent No. 685,822; British Patent No. 1,104,993 and Swiss patent 609,217. However, such methods are usually not completely efficient.

[003] Catalysts for the conversion of carbon monoxide to carbon dioxide are described, for example, in U.S. Patent Nos. 4,317,460, 4,956,330; 5,258,330; 4,956,330; 5,050,621; and 5,258,340, as well as in British Patent No. 1,315,374. The disadvantages of incorporating a conventional catalyst into a cigarette include the large quantities of oxidant that need to be incorporated into the filter to achieve considerable reduction of

carbon monoxide. Moreover, if the ineffectiveness of the heterogeneous reaction is taken into account, the amount of the oxidant required would be even larger.

[004] Metal oxides, such as iron oxide have also been incorporated into cigarettes for various purposes. See, for example, International Publications WO 87/06104 and WO 00/40104, as well as U.S. Patent Nos. 3,807,416 and 3,720,214. Iron oxide has also been proposed for incorporation into tobacco articles, for a variety of other purposes. For example, iron oxide has been described as particulate inorganic filler (*e.g.* U.S. Patent Nos. 4,197,861; 4,195,645; and 3,931,824), as a coloring agent (*e.g.* U.S. Patent No. 4,119,104) and in powder form as a burn regulator (*e.g.* U.S. Patent No. 4,109,663). In addition, several patents describe treating filler materials with powdered iron oxide to improve taste, color and/or appearance (*e.g.* U.S. Patent Nos. 6,095,152; 5,598,868; 5,129,408; 5,105,836 and 5,101,839). However, the prior attempts to make cigarettes incorporating metal oxides, such as FeO or Fe₂O₃, have not led to the effective reduction of carbon monoxide in mainstream smoke.

[005] Despite the developments to date, there remains a need for improved and more efficient methods and compositions for reducing the amount of carbon monoxide in the mainstream smoke of a cigarette during smoking. Preferably, such methods and compositions should not involve expensive or time consuming manufacturing and/or processing steps. More preferably, it should be possible to catalyze or oxidize carbon monoxide not only in the filter region of the cigarette, but also along the entire length of the cigarette during smoking.

SUMMARY

[006] The invention provides cut filler compositions, cigarettes, methods for making cigarettes and methods for smoking cigarettes that involve the use of an oxyhydroxide compound, which is capable of decomposing to form at least one product capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide.

[007] One embodiment of the invention relates to a cut filler composition comprising tobacco and an oxyhydroxide compound, wherein during combustion of the cut filler composition, the oxyhydroxide compound is capable of decomposing to form at least one product capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide.

[008] Another embodiment of the invention relates to a cigarette comprising a tobacco rod, wherein the tobacco rod comprises a cut filler composition comprising tobacco and an oxyhydroxide compound. During smoking of the cigarette, the oxyhydroxide compound is capable of decomposing to form at least one product capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide. The cigarette preferably comprises from about 5 mg to about 200 mg of the oxyhydroxide compound per cigarette, and more preferably from about 40 mg to about 100 mg of the oxyhydroxide compound per cigarette.

[009] A further embodiment of the invention relates to a method of making a cigarette, comprising (i) adding an oxyhydroxide compound to a cut filler, wherein the oxyhydroxide compound is capable of decomposing during the smoking of the cigarette to form at least one product capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide; (ii) providing the cut filler comprising the oxyhydroxide compound to a cigarette making machine to form a tobacco rod; and (iii) placing a paper wrapper around the tobacco rod to form the cigarette. The cigarette thus produced preferably comprises from about 5 mg to about 200 mg of the oxyhydroxide compound per cigarette, and more preferably from about 40 mg to about 100 mg of the oxyhydroxide compound per cigarette.

[0010] Yet another embodiment of the invention relates to a method of smoking the cigarette described above, which involves lighting the cigarette to form smoke and inhaling the smoke, wherein during the smoking of the cigarette, the oxyhydroxide compound is

capable of decomposing to form at least one product capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide.

[0011] In a preferred embodiment of the invention, the oxyhydroxide compound is capable of decomposing to form at least one product capable of acting as both an oxidant for the conversion of carbon monoxide to carbon dioxide and as a catalyst for the conversion of carbon monoxide to carbon dioxide. Preferred oxyhydroxide compounds include, but are not limited to: FeOOH , AlOOH , TiOOH , and mixtures thereof, with FeOOH being particularly preferred. Preferably, the oxyhydroxide compound is capable of decomposing to form at least one product selected from the group consisting of Fe_2O_3 , Al_2O_3 , TiO_2 , and mixtures thereof. Preferably, the product formed from the decomposition of the oxyhydroxide during combustion of the cut filler composition is present in an amount effective to convert at least 50% of the carbon monoxide to carbon dioxide.

[0012] In yet another preferred embodiment, the oxyhydroxide compound and/or the product formed from the decomposition of the oxyhydroxide during combustion of the cut filler composition is in the form of nanoparticles, preferably having an average particle size less than about 500 nm, more preferably having an average particle size less than about 100 nm, more preferably having an average particle size less than about 50 nm, and most preferably having an average particle size less than about 5 nm.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Various features and advantages of this invention will be apparent upon consideration of the following detailed description, taken in conjunction with the accompanying drawings, in which:

[0014] FIG. 1 depicts the temperature dependence of the Gibbs Free Energy and Enthalpy for the oxidation reaction of carbon monoxide to form carbon dioxide.

[0015] FIG. 2 depicts the temperature dependence for the conversion of carbon dioxide to carbon monoxide by carbon.

[0016] FIG. 3 depicts a comparison of the Gibbs Energy changes of various reactions among carbon, oxygen, carbon monoxide, carbon dioxide, and hydrogen gas.

[0017] FIG. 4 depicts the percentage conversion of carbon dioxide to carbon monoxide at different temperatures, by carbon and hydrogen respectively.

[0018] FIG. 5 depicts the Gibbs Energy changes for several reactions involving Fe(III) and/or carbon monoxide.

[0019] FIG. 6 depicts the conversion of carbon monoxide to carbon dioxide by Fe_2O_3 and Fe_3O_4 respectively, over a range of temperatures.

[0020] FIG. 7 depicts the Gibbs Energy change for the decomposition of FeOOH , over a range of temperatures.

[0021] FIG. 8 depicts the Enthalpy Changes of FeOOH decomposition and Fe_2O_3 reduction, respectively, over a range of temperatures.

[0022] FIG. 9 depicts a comparison between the catalytic activity of Fe_2O_3 nanoparticles (NANOCAT® Superfine Iron Oxide (SFIO) from MACH I, Inc., King of Prussia, PA) having an average particle size of about 3 nm, versus Fe_2O_3 powder (from Aldrich Chemical Company) having an average particle size of about $5\mu\text{m}$.

[0023] FIGs. 10 depicts the combustion zone of a cigarette during smoking (where the Fe_2O_3 nanoparticles act as an oxidant) and the pyrolysis region of a cigarette during smoking (where the Fe_2O_3 nanoparticles act as a catalyst), as well as the relevant reactions that occur in those regions.

[0024] FIG. 11A depicts the combustion zone, the pyrolysis/distillation zone, and the condensation/filtration zone, and FIGs. 11B, 11C and 11D depict the relative levels of oxygen, carbon dioxide and carbon monoxide respectively, along the length of the cigarette during smoking.

[0025] FIG. 12 depicts a schematic of a quartz flow tube reactor.

[0026] FIG. 13 depicts the temperature dependence on the production of carbon monoxide, carbon dioxide and oxygen, when using Fe_2O_3 nanoparticles as the catalyst for the oxidation of carbon monoxide by oxygen to produce carbon dioxide.

[0027] FIG. 14 illustrates the relative production of carbon monoxide, carbon dioxide and oxygen, when using Fe_2O_3 nanoparticles as an oxidant for the reaction of Fe_2O_3 with carbon monoxide to produce carbon dioxide and FeO .

[0028] FIGs. 15A and 15B illustrate the reaction orders of carbon monoxide and carbon dioxide with Fe_2O_3 as a catalyst.

[0029] FIG. 16 depicts the measurement of the activation energy and the pre-exponential factor for the reaction of carbon monoxide with oxygen to produce carbon dioxide, using Fe_2O_3 nanoparticles as a catalyst for the reaction.

[0030] FIG. 17 depicts the temperature dependence for the conversion rate of carbon monoxide, for flow rates of 300mL/min and 900 mL/min respectively.

[0031] FIG. 18 depicts contamination and deactivation studies for water wherein curve 1 represents the condition for 3 % H_2O and curve 2 represents the condition for no H_2O .

[0032] FIG. 19 depicts a flow tube reactor setup to simulate a cigarette in evaluating different catalysts and catalyst precursors.

[0033] FIG. 20 depicts the relative amounts of carbon monoxide and carbon dioxide production without a catalyst present.

[0034] FIG. 21 depicts the relative amounts of carbon monoxide and carbon dioxide production with a Fe_2O_3 nanoparticle catalyst present.

DETAILED DESCRIPTION

[0035] The invention provides cut filler compositions, cigarettes, methods for making cigarettes and methods for smoking cigarettes which involve the use of an oxyhydroxide compound that is capable of decomposing during smoking to form at least one product capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide. Through the invention, the amount of carbon monoxide in mainstream smoke can be reduced, thereby also reducing the amount of carbon monoxide reaching the smoker and/or given off as second-hand smoke.

[0036] The term "mainstream" smoke refers to the mixture of gases passing down the tobacco rod and issuing through the filter end, *i.e.* the amount of smoke issuing or drawn from the mouth end of a cigarette during smoking of the cigarette. The mainstream smoke contains smoke that is drawn in through both the lit region of the cigarette, as well as through the cigarette paper wrapper.

[0037] The total amount of carbon monoxide present in mainstream smoke and formed during smoking comes from a combination of three main sources: thermal decomposition (about 30%), combustion (about 36%) and reduction of carbon dioxide with carbonized tobacco (at least 23%). Formation of carbon monoxide from thermal decomposition starts at a temperature of about 180°C, and finishes at around 1050°C, and

is largely controlled by chemical kinetics. Formation of carbon monoxide and carbon dioxide during combustion is controlled largely by the diffusion of oxygen to the surface (k_a) and the surface reaction (k_b). At 250°C, k_a and k_b , are about the same. At 400°C, the reaction becomes diffusion controlled. Finally, the reduction of carbon dioxide with carbonized tobacco or charcoal occurs at temperatures around 390°C and above. Besides the tobacco constituents, the temperature and the oxygen concentration are the two most significant factors affecting the formation and reaction of carbon monoxide and carbon dioxide.

[0038] While not wishing to be bound by theory, it is believed that the oxyhydroxide compounds decompose under conditions for the combustion of the cut filler or the smoking of the cigarette to produce either catalyst or oxidant compounds, which target the various reactions that occur in different regions of the cigarette during smoking. During smoking there are three distinct regions in a cigarette: the combustion zone, the pyrolysis/distillation zone, and the condensation/filtration zone. First, the "combustion region" is the burning zone of the cigarette, produced during smoking of the cigarette, usually at the lit end of a cigarette. The temperature in the combustion zone ranges from about 700°C to about 950°C, and the heating rate can go as high as 500°C/second. The concentration of oxygen is low in this region, since it is being consumed in the combustion of tobacco to produce carbon monoxide, carbon dioxide, water vapor, and various organics. This reaction is highly exothermic and the heat generated here is carried by gas to the pyrolysis/distillation zone. The low oxygen concentrations coupled with the high temperature in the combustion region leads to the reduction of carbon dioxide to carbon monoxide by the carbonized tobacco. In the combustion region, it is desirable to use an oxyhydroxide that decomposes to form an oxidant *in situ*, which will convert carbon monoxide to carbon dioxide in the absence of oxygen. The oxidation reaction begins at around 150°C, and reaches maximum activity at temperatures higher than about 460°C.

[0039] Next, the "pyrolysis region" is the region behind the combustion region, where the temperatures range from about 200°C to about 600°C. This is where most of the

carbon monoxide is produced. The major reaction in this region is the pyrolysis (*i.e.* the thermal degradation) of the tobacco that produces carbon monoxide, carbon dioxide, smoke components, and charcoal using the heat generated in the combustion zone. There is some oxygen present in this zone, and thus it is desirable to use an oxyhydroxide that decomposes to produce a catalyst *in situ* for the oxidation of carbon monoxide to carbon dioxide. The catalytic reaction begins at 150°C and reaches maximum activity around 300°C. In a preferred embodiment, the catalyst may also retain oxidant capability after it has been used as a catalyst, so that it can also function as an oxidant in the combustion region as well.

[0040] Finally, there is the condensation/filtration zone, where the temperature ranges from ambient to about 150°C. The major process is the condensation/filtration of the smoke components. Some amount of carbon monoxide and carbon dioxide diffuse out of the cigarette and some oxygen diffuses into the cigarette. However, in general, the oxygen level does not recover to the atmospheric level.

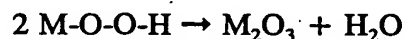
[0041] In commonly-assigned U.S. application number 09/942,881, filed August 31, 2001, and entitled "Oxidant/Catalyst Nanoparticles to Reduce Carbon Monoxide in the Mainstream Smoke of a Cigarette", various oxidant/catalyst nanoparticles are described for reducing the amount of carbon monoxide in mainstream smoke. The disclosure of this application is hereby incorporated by reference in its entirety. While the use of these catalysts reduce the amount of carbon monoxide in mainstream smoke during smoking, it is further desirable to minimize or prevent contamination and/or deactivation of catalysts used in the cigarette filler, particularly over long periods of storage. One potential way of achieving this result is to use an oxyhydroxide compound to generate the catalyst or oxidant *in situ* during smoking of the cigarette. For instance, FeOOH decomposes to form Fe₂O₃ and water at temperatures typically reached during smoking of the cigarette, *e.g.* above about 200°C.

[0042] By "oxyhydroxide" is meant a compound containing a hydroperoxo moiety,

i.e. " —O—O—H ". Examples of oxyhydroxides include, but are not limited to: FeOOH , AlOOH , and TiOOH . Any suitable oxyhydroxide compound may be used, which is capable of decomposing, under the temperature conditions achieved during smoking of a cigarette, to produce compounds which function as an oxidant and/or as a catalyst for converting carbon monoxide to carbon dioxide. In a preferred embodiment of the invention, the oxyhydroxide forms a product that is capable of acting as both an oxidant for the conversion of carbon monoxide to carbon dioxide and as a catalyst for the conversion of carbon monoxide to carbon dioxide. It is also possible to use combinations of oxyhydroxide compounds to obtain this effect.

[0043] Preferably, the selection of an appropriate oxyhydroxide compound will take into account such factors as stability and preservation of activity during storage conditions, low cost and abundance of supply. Preferably, the oxyhydroxide will be a benign material. Further, it is preferred that the oxyhydroxide compound does not react or form unwanted byproducts during smoking.

[0044] Preferred oxyhydroxide compounds are stable when present in cut filler compositions or in cigarettes, at typical room temperature and pressure, as well as under prolonged storage conditions. Preferred oxyhydroxide compounds include inorganic oxyhydroxide compounds that decompose during smoking of a cigarette, to form metal oxides. For example, in the following reaction, M represents a metal:



[0045] Optionally, one or more oxyhydroxides may also be used as mixtures or in combination, where the oxyhydroxides may be different chemical entities or different forms of the same metal oxyhydroxides. Preferred oxyhydroxide compounds include, but are not limited to: FeOOH , AlOOH , TiOOH , and mixtures thereof, with FeOOH being particularly preferred. Other preferred oxyhydroxide compounds include those that are capable of decomposing to form at least one product selected from the group consisting of

Fe_2O_3 , Al_2O_3 , TiO_2 , and mixtures thereof. Particularly preferred oxyhydroxides include FeOOH , particularly in the form of α - FeOOH (goethite); however, other forms of FeOOH such as γ - FeOOH (lepidocrocite), β - FeOOH (akaganeite), and δ' - FeOOH (feroxyhite) may also be used. Other preferred oxyhydroxides include γ - AlOOH (boehmite) and α - AlOOH (diaspore). The oxyhydroxide compound may be made using any suitable technique, or purchased from a commercial supplier, such as Aldrich Chemical Company, Milwaukee, Wisconsin.

[0046] FeOOH is preferred because it produces Fe_2O_3 upon thermal degradation. Fe_2O_3 is a preferred catalyst/oxidant because it is not known to produce any unwanted byproducts, and will simply be reduced to FeO or Fe after the reaction. Further, when Fe_2O_3 is used as the oxidant/catalyst, it will not be converted to an environmentally hazardous material. In addition, use of a precious metal can be avoided, as both Fe_2O_3 and Fe_2O_3 nanoparticles are economical and readily available. Moreover, Fe_2O_3 is capable of acting as both an oxidant for the conversion of carbon monoxide to carbon dioxide and as a catalyst for the conversion of carbon monoxide to carbon dioxide.

[0047] In selecting an oxyhydroxide compound, various thermodynamic considerations may be taken into account, to ensure that oxidation and/or catalysis will occur efficiently, as will be apparent to the skilled artisan. For reference, FIG. 1 shows a thermodynamic analysis of the Gibbs Free Energy and Enthalpy temperature dependence for the oxidation of carbon monoxide to carbon dioxide. FIG. 2 shows the temperature dependence of the percentage of carbon dioxide conversion with carbon to form carbon monoxide.

[0048] The following thermodynamic equations are useful for analyzing the limits of the relevant reactions and their dependence on temperature:

At $p=1$ atm,

$$C_p = a + b \cdot y + c \cdot y^2 + d \cdot y^2 \quad \text{in J/(mol} \cdot \text{K)}$$

$$H = 10^3 [H^\ddagger + a \cdot y + (b/2) \cdot y^2 - c \cdot y^1 + (d/3) \cdot y^3] \quad \text{in J/mol}$$

$$S = S^\ddagger + a \cdot \ln(T/K) + b \cdot y - (c/2) \cdot y^2 + (d/2) \cdot y^2 \quad \text{in J/(mol} \cdot \text{K)}$$

$$G = 10^3 [H^\ddagger - S^\ddagger \cdot y - a \cdot y \cdot \ln(T-1) - (b/2) \cdot y^2 - (c/2) \cdot y^3 - (d/6) \cdot y^3] \quad \text{in J/mol}$$

where $y = 10^3 + T$

[0049] The equilibrium constant K_e can be calculated from ΔG : $K_e = \exp [-\Delta G/(R \cdot T)]$. For some reactions, or the percentages of the conversions, α , can be calculated from K_e .

Table 1. Thermodynamic parameters and constants.

	A	B	C	d	H^\ddagger	S^\ddagger
C (graphite)	0.109	38.940	-0.146	-17.385	-2.101	-6.546
CO (gas)	30.962	2.439	-0.280		-120.809	18.937
CO ₂ (gas)	51.128	4.368	-1.469		-413.886	-87.937
O ₂ (gas)	29.154	6.477	-0.184	-1.017	-9.589	36.116
FeO (solid)	48.794	8.372	-0.289		-281.844	-222.719
Fe ₃ O ₄ (solid)	91.558	201.970			-1151.755	-435.650
Fe ₂ O ₃ (solid)	98.278	77.818	-1.485		-861.153	-504.059
FeOOH (solid)	49.371	83.680			-576.585	-245.871
H ₂ O (vapor)	34.376	7.841	-0.423		-253.871	-11.75
H ₂ (gas)	26.882	3.568	0.105		-7.823	-22.966

[0050] FIG. 3 shows a comparison of the Gibbs free energy changes of various reactions involving carbon, carbon monoxide, carbon dioxide, and oxygen. As shown in the chart, both the oxidation reaction of carbon to carbon monoxide, and the oxidation of carbon monoxide to carbon dioxide are thermodynamically favorable. The oxidation of carbon to carbon dioxide is more favorable, according to the ΔG of the reaction. The oxidation of carbon monoxide to carbon dioxide is also strongly favorable. Therefore, in the combustion zone, carbon dioxide should be the dominating product unless there is a shortage of oxygen. As shown in FIG. 3, under oxygen deficient conditions, carbon dioxide can be reduced to carbon monoxide by carbon. There is also the possibility that the carbon dioxide may be reduced to carbon monoxide by hydrogen, since hydrogen is also generated in the combustion process.

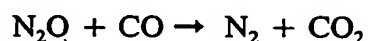
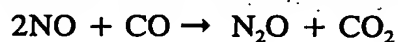
[0051] FIG. 4 shows the percentage of carbon dioxide converted to carbon monoxide, by carbon and hydrogen respectively, under oxygen deficient conditions at different temperatures. The reduction of carbon dioxide by carbon starts at about 700 K, which is very close to the experimental observation of about 400°C. At the combustion zone, where the temperature is about 800°C, as shown in FIG. 4, about 80% of carbon dioxide will be reduced to carbon monoxide. While the carbon dioxide may be reduced by hydrogen gas, this reaction is unlikely as hydrogen gas diffuses out of the cigarette quickly.

[0052] FIGs. 5-8 illustrate the effect of using iron compounds as oxidant and/or catalyst in cigarettes for the oxidation of carbon monoxide to carbon dioxide. As shown in FIG. 5, the oxidation of carbon monoxide to carbon dioxide is energetically favorable for Fe_2O_3 , even at room temperature. At higher temperature, the oxidation of carbon by Fe_2O_3 also becomes energetically favorable. Similar trends are observed for the reactions of Fe_3O_4 with carbon and carbon monoxide, but generally the reactions with Fe_3O_4 are less energetically favorable than with Fe_2O_3 . The competition with carbon with carbon monoxide should not be significant since the reaction with carbon is solid to solid reaction that usually cannot proceed unless the temperature is very high.

[0053] FIG. 6 shows the temperature dependence for the conversion of carbon monoxide to carbon dioxide. With Fe_2O_3 , the carbon monoxide to carbon dioxide conversion percentage can reach almost 100% in a broad temperature range starting with the ambient temperature. Fe_3O_4 is less effective. It is desirable to use freshly prepared Fe_2O_3 to maintain the high activity. One possible way to do this is generating the Fe_2O_3 *in situ* from an iron oxyhydroxide, such as FeOOH . While FeOOH is stable at ambient temperature, it will thermally decompose to form Fe_2O_3 and water, at temperatures around 200°C . Thermodynamic calculations confirm that decomposition is an energetically favorable process, as shown in FIG. 7.

[0054] Another advantage of using FeOOH instead of Fe_2O_3 as the oxidant is that the decomposition of FeOOH is endothermic over a broad temperature range, as shown in FIG. 8. Thus, the heat consumed in the decomposition is more than the heat generated by the reduction of Fe_2O_3 by carbon monoxide. The net result is a slight decrease of the temperature in the combustion zone, which also contributes to the reduction of carbon monoxide concentration in mainstream smoke.

[0055] During combustion, NO is also produced in mainstream smoke at a concentration of about 0.45 mg/cigarette. However, NO can be reduced by carbon monoxide according to the following reactions:



Iron oxide, either in the reduced form of Fe_3O_4 or in the oxidized form of Fe_2O_3 , acts as a good catalyst for these two reactions at temperatures around about 300°C . Therefore, the addition of iron oxide or its generation *in situ* in the cigarette during smoking could potentially minimize the concentration of NO in mainstream smoke as well.

[0056] In a preferred embodiment of the invention, the oxyhydroxide compound and/or the product formed from the decomposition of the oxyhydroxide during combustion or smoking is in the form of nanoparticles. By "nanoparticles" is meant that the particles

have an average particle size of less than a micron. The preferred average particle size is less than about 500 nm, more preferably less than about 100 nm, even more preferably less than about 50 nm, and most preferably less than about 5 nm. Preferably, the oxyhydroxide compound and/or the product formed from the decomposition of the oxyhydroxide during combustion or smoking has a surface area from about 20 m²/g to about 400 m²/g, or more preferably from about 200 m²/g to about 300 m²/g.

[0057] FIG. 9 shows a comparison between the catalytic activity of Fe₂O₃ nanoparticles (NANOCAT® Superfine Iron Oxide (SFIO) from MACH I, Inc., King of Prussia, PA) having an average particle size of about 3 nm, versus Fe₂O₃ powder (from Aldrich Chemical Company) having an average particle size of about 5 μm. The Fe₂O₃ nanoparticles show a much higher percentage of conversion of carbon monoxide to carbon dioxide than the Fe₂O₃ having an average particle size of about 5 μm. Such results may also be achieved using FeOOH particles that decompose during smoking to produce Fe₂O₃ nanoparticles *in situ*.

[0058] As shown schematically in FIG. 10, the Fe₂O₃ nanoparticles act as a catalyst in the pyrolysis zone, and act as an oxidant in the combustion region. FIG. 11A shows various temperature zones in a lit cigarette, and FIGs. 11B, 11C and 11D show the respective amounts of oxygen, carbon dioxide and carbon monoxide in each region of the cigarette during smoking. The oxidant/catalyst dual function and the reaction temperature range make Fe₂O₃ a preferred oxidant/catalyst to be generated *in situ*. Also, during the smoking of the cigarette, the Fe₂O₃ may be used initially as a catalyst (*i.e.* in the pyrolysis zone), and then as an oxidant (*i.e.* in the combustion region).

[0059] Various experiments to further study thermodynamic and kinetics of various catalysts were conducted using a quartz flow tube reactor. The kinetics equation governing these reactions is as follows:

$$\ln (1-x) = -A_0 e^{-(E_a/RT)} \cdot (s \cdot l/F)$$

where the variables are defined as follows:

x = the percentage of carbon monoxide converted to carbon dioxide

A_0 = the pre-exponential factor, $5 \times 10^{-6} \text{ s}^{-1}$

R = the gas constant, $1.987 \times 10^{-3} \text{ kcal}/(\text{mol} \cdot \text{K})$

E_a = activation energy, 14.5 kcal/mol

s = cross section of the flow tube, 0.622 cm^2

l = length of the catalyst, 1.5 cm

F = flow rate, in cm^3/s

A schematic of a quartz flow tube reactor, suitable for carrying out such studies, is shown in FIG. 12. Helium, oxygen/helium and/or carbon monoxide/helium mixtures may be introduced at one end of the reactor. A quartz wool dusted with catalyst or catalyst precursor, such as Fe_2O_3 or FeOOH , is placed within the reactor. The products exit the reactor at a second end, which comprises an exhaust and a capillary line to a Quadrupole Mass Spectrometer ("QMS"). The relative amounts of products can thus be determined for a variety of reaction conditions.

[0060] FIG. 13 is a graph of temperature versus QMS intensity for a test wherein Fe_2O_3 nanoparticles are used as a catalyst for the reaction of carbon monoxide with oxygen to produce carbon dioxide. In the test, about 82 mg of Fe_2O_3 nanoparticles are loaded in the quartz flow tube reactor. Carbon monoxide is provided at 4% concentration in helium at a flow rate of about 270 mL/min, and oxygen is provided at 21% concentration in helium at a flow rate of about 270 mL/min. The heating rate is about 12.1 K/min. As shown in this graph, Fe_2O_3 nanoparticles are effective at converting carbon monoxide to carbon dioxide at temperatures above around 225°C.

[0061] FIG. 14 is a graph of time versus QMS intensity for a test wherein Fe_2O_3 nanoparticles are studied as an oxidant for the reaction of Fe_2O_3 with carbon monoxide to produce carbon dioxide and FeO . In the test, about 82 mg of Fe_2O_3 nanoparticles are loaded in the quartz flow tube reactor. Carbon monoxide is provided at 4% concentration

in helium at a flow rate of about 270 mL/min, and the heating rate is about 137 K/min to a maximum temperature of 460 °C. As suggested by data shown in FIGs. 13 and 14, Fe_2O_3 nanoparticles are effective in conversion of carbon monoxide to carbon dioxide under conditions similar to those during smoking of a cigarette.

[0062] FIGs. 15A and 15B are graphs showing the reaction orders of carbon monoxide and carbon dioxide with Fe_2O_3 as a catalyst. FIG. 16 depicts the measurement of the activation energy and the pre-exponential factor for the reaction of carbon monoxide with oxygen to produce carbon dioxide, using Fe_2O_3 nanoparticles as a catalyst for the reaction. A summary of activation energies is provided in Table 2.

Table 2. Summary of the Activation Energies and Pre-exponential Factors

	Flow Rate (mL/min)	CO%	O ₂ %	A _o (s ⁻¹)	E _a (kcal/mol)
1	300	1.32	1.34	1.8 x 10 ⁷	14.9
2	900	1.32	1.34	8.2 x 10 ⁶	14.7
3	1000	3.43	20.6	2.3 x 10 ⁶	13.5
4	500	3.43	20.6	6.6 x 10 ⁶	14.3
5	250	3.42	20.6	2.2 x 10 ⁷	15.3
AVG.				5 x 10 ⁶	14.5
Ref.					
1	Gas Phase		—		39.7
2	2% Au/TiO ₂				7.6
3	2.2% Pd/Al ₂ O ₃				9.6

[0063] FIG. 17 depicts the temperature dependence for the conversion rate of carbon monoxide using 50 mg Fe_2O_3 nanoparticles as catalyst in the quartz tube reactor, for flow rates of 300mL/min and 900 mL/min respectively.

[0064] FIG. 18 depicts contamination and deactivation studies for water using 50 mg Fe_2O_3 nanoparticles as catalyst in the quartz tube reactor. As can be seen from the graph, compared to curve 1 (without water), the presence of up to 3% water (curve 2) has little effect on the ability of Fe_2O_3 nanoparticles to convert carbon monoxide to carbon dioxide.

[0065] FIG. 19 shows a flow tube reactor to simulate a cigarette in evaluating different nanoparticle catalysts. Table 3 shows a comparison between the ratio of carbon monoxide to carbon dioxide, and the percentage of oxygen depletion when using Al_2O_3 and Fe_2O_3 nanoparticles.

Table 3. Comparison between Al_2O_3 , and Fe_2O_3 nanoparticles

Nanoparticle	CO/CO ₂	O ₂ Depletion (%)
None	0.51	48
Al_2O_3	0.40	60
Fe_2O_3	0.23	100

In the absence of nanoparticles, the ratio of carbon monoxide to carbon dioxide is about 0.51 and the oxygen depletion is about 48%. The data in Table 3 illustrates the improvement obtained by using nanoparticles. The ratio of carbon monoxide to carbon dioxide drops to 0.40 and 0.23 for Al_2O_3 and Fe_2O_3 nanoparticles, respectively. The oxygen depletion increases to 60% and 100% for Al_2O_3 and Fe_2O_3 nanoparticles, respectively.

[0066] FIG. 20 is a graph of temperature versus QMS intensity in a test which shows the amounts of carbon monoxide and carbon dioxide production without a catalyst present. FIG. 21 is a graph of temperature versus QMS intensity in a test which shows the amounts of carbon monoxide and carbon dioxide production when using Fe_2O_3 nanoparticles as a catalyst. As can be seen by comparing FIG. 20 and FIG. 21, the presence of Fe_2O_3 nanoparticles increases the ratio of carbon dioxide to carbon monoxide present, and decreases the amount of carbon monoxide present.

[0067] The oxyhydroxide compounds, as described above, may be provided along the length of a tobacco rod by distributing the oxyhydroxide compounds on the tobacco or incorporating them into the cut filler tobacco using any suitable method. The oxyhydroxide compounds may be provided in the form of a powder or in a solution in the form of a dispersion, for example. In a preferred method, the oxyhydroxide compounds in the form of a dry powder are dusted on the cut filler tobacco. The oxyhydroxide compounds may also be present in the form of a solution or dispersion, and sprayed on the cut filler tobacco. Alternatively, the tobacco may be coated with a solution containing the oxyhydroxide compounds. The oxyhydroxide compounds may also be added to the cut filler tobacco stock supplied to the cigarette making machine or added to a tobacco rod prior to wrapping cigarette paper around the cigarette rod.

[0068] The oxyhydroxide compounds will preferably be distributed throughout the tobacco rod portion of a cigarette and optionally the cigarette filter. By providing the oxyhydroxide compounds throughout the entire tobacco rod, it is possible to reduce the amount of carbon monoxide throughout the cigarette, and particularly at both the combustion region and in the pyrolysis zone.

[0069] The amount of oxyhydroxide compound to be used may be determined by routine experimentation. Preferably, the product formed from the decomposition of the oxyhydroxide during combustion of the cut filler composition is present in an amount effective to convert at least 50% of the carbon monoxide to carbon dioxide. Preferably, the

amount of the oxyhydroxide will be from about a few milligrams, for example, 5 mg/cigarette, to about 200 mg/cigarette. More preferably, the amount of oxyhydroxide will be from about 40 mg/cigarette to about 100 mg/cigarette.

[0070] One embodiment of the invention relates to a cut filler composition comprising tobacco and at least one oxyhydroxide compound, as described above, which is capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide. Any suitable tobacco mixture may be used for the cut filler. Examples of suitable types of tobacco materials include flue-cured, Burley, Maryland or Oriental tobaccos, the rare or specialty tobaccos, and blends thereof. The tobacco material can be provided in the form of tobacco lamina; processed tobacco materials such as volume expanded or puffed tobacco, processed tobacco stems such as cut-rolled or cut-puffed stems, reconstituted tobacco materials; or blends thereof. The invention may also be practiced with tobacco substitutes.

[0071] In cigarette manufacture, the tobacco is normally employed in the form of cut filler, *i.e.* in the form of shreds or strands cut into widths ranging from about 1/10 inch to about 1/20 inch or even 1/40 inch. The lengths of the strands range from between about 0.25 inches to about 3.0 inches. The cigarettes may further comprise one or more flavorants or other additives (*e.g.* burn additives, combustion modifying agents, coloring agents, binders, etc.) known in the art.

[0072] Another embodiment of the invention relates to a cigarette comprising a tobacco rod, wherein the tobacco rod comprises cut filler having at least one oxyhydroxide compound, as described above, which is capable of decomposing during smoking to produce a product that is capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide. A further embodiment of the invention relates to a method of making a cigarette, comprising (i) adding an oxyhydroxide compound to a cut filler, wherein the oxyhydroxide compound is capable of decomposing during smoking to produce a product

that is capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide; (ii) providing the cut filler comprising the oxyhydroxide compound to a cigarette making machine to form a tobacco rod; and (iii) placing a paper wrapper around the tobacco rod to form the cigarette.

[0073] Techniques for cigarette manufacture are known in the art. Any conventional or modified cigarette making technique may be used to incorporate the oxyhydroxide compounds. The resulting cigarettes can be manufactured to any desired specification using standard or modified cigarette making techniques and equipment. Typically, the cut filler composition of the invention is optionally combined with other cigarette additives, and provided to a cigarette making machine to produce a tobacco rod, which is then wrapped in cigarette paper, and optionally tipped with filters.

[0074] The cigarettes of the invention may range from about 50 mm to about 120 mm in length. Generally, a regular cigarette is about 70 mm long, a "King Size" is about 85 mm long, a "Super King Size" is about 100 mm long, and a "Long" is usually about 120 mm in length. The circumference is from about 15 mm to about 30 mm in circumference, and preferably around 25 mm. The packing density is typically between the range of about 100 mg/cm³ to about 300 mg/cm³, and preferably 150 mg/cm³ to about 275 mg/cm³.

[0075] Yet another embodiment of the invention relates to methods of smoking the cigarette described above, which involve lighting the cigarette to form smoke and inhaling the smoke, wherein during the smoking of the cigarette, the oxyhydroxide compound decomposes during smoking to form a compound that acts as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide.

[0076] "Smoking" of a cigarette means the heating or combustion of the cigarette to form smoke, which can be inhaled. Generally, smoking of a cigarette involves lighting one

end of the cigarette and inhaling the cigarette smoke through the mouth end of the cigarette, while the tobacco contained therein undergoes a combustion reaction. However, the cigarette may also be smoked by other means. For example, the cigarette may be smoked by heating the cigarette and/or heating using electrical heater means, as described in commonly-assigned U.S. Patent Nos. 6,053,176; 5,934,289; 5,934,289, 5,591,368 or 5,322,075, for example.

[0077] While the invention has been described with reference to preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the invention as defined by the claims appended hereto.

[0078] All of the above-mentioned references are herein incorporated by reference in their entirety to the same extent as if each individual reference was specifically and individually indicated to be incorporated herein by reference in its entirety.